

Critical Review of the La-Zn System

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Abstract: All the available data on phase equilibria, thermodynamic and structural properties of the lanthanum-zinc phases are presented and critically analysed in this paper. Although these data allow to draw an overall description of the binary system, they are not accurate enough for further extrapolations to higher order systems using computational methods. Therefore at the end of this analysis we suggest new experimental investigations to improve the description of this system.

Key Words: Lanthanum, zinc, phase diagram, thermodynamic properties.

INTRODUCTION

The low densities of Mg-Zn alloys make them very attractive for applications in transport industry. However, because of their weak mechanical performances, they cannot be used without additives. Recently it was shown that the addition of Rare Earth metals (RE) can strongly improve these mechanical properties [1-3] and thus, the studies of the RE-Mg-Zn systems become of great interest.

The optimisation of these alloys requires knowledge on thermal and chemical stabilities and consequently, on phase diagrams. For systems containing more than four constituents, the phase equilibria are generally calculated by using the CalPhaD method. However, these calculations need accurate experimental information on the constitutive binary and ternary systems.

The aim of this work is to gather all the information reported in literature on the La-Zn system, to critically analyse these data and to suggest further experimental investigations that are required to provide a more accurate description of the La-Zn system.

SOLID PHASES

Five compounds, namely LaZn, LaZn₂, LaZn₄, LaZn₈ and LaZn₁₃ are reported in the Massalski's La-Zn phase diagram [4] which is mainly drawn from Rolla *et al.* data [5]. However, a comprehensive analysis of the literature shows the identification of eight compounds, namely LaZn, LaZn₂, LaZn₄, LaZn₅, La₃Zn₂₂, La₂Zn₁₇, LaZn₁₁, LaZn₁₃. Structural data and melting points of the intermediate phases of the La-Zn system are reported in Table 1.

The available information can be summarized as follows.

LaZn (50 at. % Zn) crystallizes in a fcc structure (CsCl-type) which was first resolved by Iandelli *et al.* [6]. The cell parameters were determined by several authors [6-7] within 2% of agreement.

According to Rolla *et al.* this phase congruently melts at 1088K [5].

LaZn₂ (66.67 at. % Zn) was first reported by Rolla *et al.* [5]. Fornasini *et al.* [8] identified the crystal structure to be similar to that of the CeCu₂ Laves phase. The cell parameters were determined by Fornasini *et al.* [8] and Veleckis *et al.* [9] within 0.5% of agreement.

A congruent melting was evidenced for this phase [5, 10]. Depending on the authors, two temperatures were reported (1128 K [5] and 1125 K [10]).

LaZn₄ (80 at. % Zn) was first identified in 1941 by Rolla *et al.* [5]. Later on, in 1961, Gschneider [11] reported the existence of a new compound (LaZn₅) which is closed to LaZn₄ in composition, though without mentioning the latter compound. A further analysis [12] showed that both LaZn₄ and LaZn₅ coexist.

The crystalline structure of LaZn₄ was described by Bruzzone *et al.* [12] as "probably an orthorhombic distortion of the BaAl₄-type" structure.

Combining thermal analysis measurements and Tamman's method, Rolla *et al.* [5] determined an invariant peritectic decomposition of that phase at 1144 K.

LaZn₅ (83.3 at. % Zn) crystallizes in the CaCu₅-type hexagonal structure [13]. By analogy with the Ce-Zn system, Veleckis *et al.* [9] suggested LaZn_{5,25} as being the exact stoichiometry for this phase.

Schramm [14] performed differential thermal analysis on alloys with compositions ranging from 80.5 to 87.1 at. % Zn. Both on heating and cooling, he clearly showed the existence of an invariant reaction at 1137 K. This transition could be associated either to the LaZn₄ or the LaZn₅ decompositions.

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Table 1. Literature Data on the Intermediate Solid Phases of the La-Zn System

Phase	at. % Zn	Melting Point (K)	Space Group (Number)	Cell Parameters (Å)			Ref.
				a	b	c	
LaZn	50.0	1088	-	-	-	-	[5]
			Pm-3m (221)	3.75(2)	-	-	[6]
			Pm-3m (221)	3.760(5)	-	-	[7]
LaZn ₂	66.7	1128	-	-	-	-	[5]
		1125	-	-	-	-	[10]
			Imma (74)	4.689	7.638	7.593	[8]
			Imma (74)	4.67(7)	7.61(5)	7.55(2)	[9]
LaZn ₄	80.0	1144*	-	-	-	-	[5]
			Cmc21(36), Cmcn(63)	6.11	6.33	10.29	[12]
LaZn ₅	83.3	1137*	-	-	-	-	[5, 14]
			P6/mmm (191)	5.471	-	4.264	[9]
			P6/mmm (191)	5.416	-	4.217	[14]
La ₃ Zn ₂₂	88.0	1205*	-	-	-	-	[14]
			I4 ₁ /amd (141)	8.97(1)	-	21.48(5)	[15]
La ₂ Zn ₁₇	89.5	1247	-	-	-	-	[5]
		1235	-	-	-	-	[14]
			R-3m (166)	9.131(4)	-	13.334(5)	[16]
				(9.125)	-	(8.896)	[9]
			R-3m (166)	9.1315(3)	-	13.3340(5)	[17]
LaZn ₁₁	91.6	983*	-	-	-	-	[14]
			I4 ₁ /amd (141)	10.68	-	6.87	[18]
			I4 ₁ /amd (141)	10.686	-	6.881	[16]
LaZn ₁₃	92.8	1113*	-	-	-	-	[5]
			Fm-3c (226)	12.060(1)	-	-	[20]
				12.079-12.096			[9]
				12.096(5)	-	-	[16]

*peritectic decomposition.

If one considers that the temperature 1144K corresponds to the decomposition of LaZn₄ as reported in Ref. [5], we can assume that 1137 K is the temperature of the peritectoid decomposition of LaZn₅ following the reaction LaZn₅ = LaZn₄ + La₃Zn₂₂.

La₃Zn₂₂ (88 at. %Zn) was first described as LaZn_{7.3} by Veleckis *et al.* [9]. Later on, Kripyakevich *et al.* [15] determined the cell parameters of this phase using an analogy with the Pu₃Zn₂₂ structure. Therefore we will retain the La₃Zn₂₂ formula for this phase.

Using differential thermal analysis, Schramm [14] evidenced an invariant reaction at 1205 K for a composition around 88 at. % Zn. This thermal phenomenon can be attributed to the peritectic decomposition of La₃Zn₂₂. However, the observed temperature might be underestimated as it was determined on cooling.

La₂Zn₁₇ (89.5 at. % Zn) was first reported by Gschneider [11]. Prior to Gschneider's work two phases, namely LaZn₈ (88.8 at. % Zn) and LaZn₉ (90.0 at. % Zn), were reported around 89.5 at. % Zn. Based on an analogy with the Th-Ni system, Gschneider propose to replace LaZn₈ and LaZn₉ by La₂Zn₁₇.

Based on structural studies performed on single crystals of Ho₂Zn₁₇ and Th₂Zn₁₇, Iandelli *et al.* [16] suggested that whatever the RE element, RE₂Zn₁₇ compounds crystallize in the same structure. This assumption was confirmed by Siegrist *et al.* [17] for La₂Zn₁₇ by measuring the cell parameters of this phase. These cell parameters were also determined by Iandelli *et al.* [16] and Veleckis *et al.* [9]. Note however that Veleckis and co-workers used the Th₂Ni₁₇ structure to determine the cell parameters of La₂Zn₁₇. Hence Veleckis' parameters cannot be considered as reliable.

Schramm [14] and Rolla *et al.* [5] found a congruent melting for $\text{La}_2\text{Zn}_{17}$ at 1235 K and 1247 K respectively.

LaZn_{11} (91.6 at. % Zn) was first observed by Schramm [14]. According to Sanderson *et al.* [18], this phase crystallizes in the BaCd_{11} structure. The cell parameters were determined by Sanderson *et al.* [18] and Iandelli *et al.* [16] within 1% of agreement.

According to Schramm *et al.* [14], LaZn_{11} is stable up to 983 K. Above this temperature, LaZn_{11} peritectically decomposes to give $\text{La}_2\text{Zn}_{17}$ and liquid. Kovalevskii *et al.* [19] observed the LaZn_{11} phase at 1000 K. This is not consistent with the above mentioned Schramm proposition. However, thermal analysis measurements performed on three alloys with compositions closed to that of $\text{La}_2\text{Zn}_{17}$ and LaZn_{11} show an invariant transition at 991 K which is still not explained.

LaZn_{13} (92.8 at. % Zn) which is the zinc richest phase was first observed by Rolla *et al.* [5]. Kuz'ma *et al.* [20] showed that the structure of this phase is similar to that of the NaZn_{13} cubic phase. Veleckis *et al.* [9] determined the cell parameter of LaZn_{13} . As they found values ranging from 12.079 Å to 12.096 Å, they concluded that LaZn_{13} is not a stoichiometric phase. However, they did not define the homogeneity range with accuracy.

The cubic cell parameter of this phase was also determined by Iandelli *et al.* [16] and Kuz'ma *et al.* [20]. Iandelli's value corresponds to Veleckis' highest one while the cell parameter determined by Kuz'ma *et al.* [20] agrees within 0.2% with Veleckis' lowest one.

An invariant reaction was observed at 1113 K both by Rolla *et al.* [5] and Iandelli *et al.* [16]. This reaction is associated by the former authors to the peritectic decomposition " $\text{LaZn}_{13} = \text{La}_2\text{Zn}_{17} + \text{liquid}$ ". By contrast, the latter authors attributed this reaction to the peritectic decomposition " $\text{LaZn}_{11} = \text{La}_2\text{Zn}_{17} + \text{liquid}$ ".

As mentioned earlier in this section, an invariant transition which could not be interpreted was reported at 991 K by Schramm [14] for alloys with compositions ranging from $\text{La}_2\text{Zn}_{17}$ to LaZn_{11} .

To obtain a consistent phase diagram we could propose a peritectic transition for LaZn_{13} ($\text{liquid} + \text{La}_2\text{Zn}_{17} = \text{LaZn}_{13}$) at 1113 K and a solid-solid transformation for LaZn_{11} at 991 K ($\text{La}_2\text{Zn}_{17} + \text{LaZn}_{13} = \text{LaZn}_{11}$). However, such an interpretation is not consistent with the results of Kovalevskii *et al.* [19] who reported LaZn_{11} as a stable phase at 1000 K. As a consequence, new measurements have to be performed in the zinc richest part of the La-Zn phase diagram.

Finally, it is worthwhile to note that no solubility in pure La and Zn phases were reported in the literature.

PHASE EQUILIBRIA

All the investigations of the La-Zn phase diagram reported in literature are listed in Table 2.

Invariant Equilibria

Rolla *et al.* [5] are the only authors who investigated the lanthanum richest part of the La-Zn phase diagram. However they did not mention the two well known phase transformations of pure lanthanum, namely $\text{dhcp-La} = \text{fcc-La}$ and $\text{fcc-La} = \text{bcc-La}$ (see Ref. [21]). According to Gschneidner [11], Rolla *et al.* [5] used low purity La (98 %) for the synthesis of their alloys. This might explain why the phase transformations were not mentioned and the reported melting point of La was 100K lower than the reference melting temperature provided by [21]. Therefore, for compositions lower than 10 at. % Zn, Rolla's results are doubtful.

Twelve binary invariant equilibria were found in literature. Their characteristics are gathered in Table 3.

The melting temperatures of the intermediate phases have already been discussed in the previous section. Regarding to the additional equilibria, they correspond to four eutectics:

Eutectic 1 (liquid = fcc-La + LaZn) was observed by Rolla *et al.* [5] at 803 K. Using Tamman's method, the eutectic composition was estimated to amount to 22 at. %.

Eutectic 2 (liquid = LaZn + LaZn_2) was found by Rolla *et al.* [5] at 1033 K with a eutectic composition of 56.5 at. % Zn. A weak thermal effect was observed by Michel *et al.* [10] at 1047 K for an alloy containing 66.66 at. % Zn. This effect was attributed to an allotropic transformation in the LaZn_2 compound. However, since such transformations were never reported so far for REZn₂ type compounds, this thermal effect can be attributed to the eutectic 2 provided that the composition of the sample was richer in lanthanum than expected. Because of this discrepancy, the temperature of this eutectic should to be checked.

Eutectic 3 (liquid = $\text{LaZn}_2 + \text{LaZn}_4$) was observed by Rolla *et al.* [5] on several alloys. The corresponding temperatures show a large dispersion (Fig. 1). The values range from 1038 K to 1066 K with an average value of 1055 K. Using Tamman's method, the eutectic composition was estimated to amount to 73.4 at. % Zn.

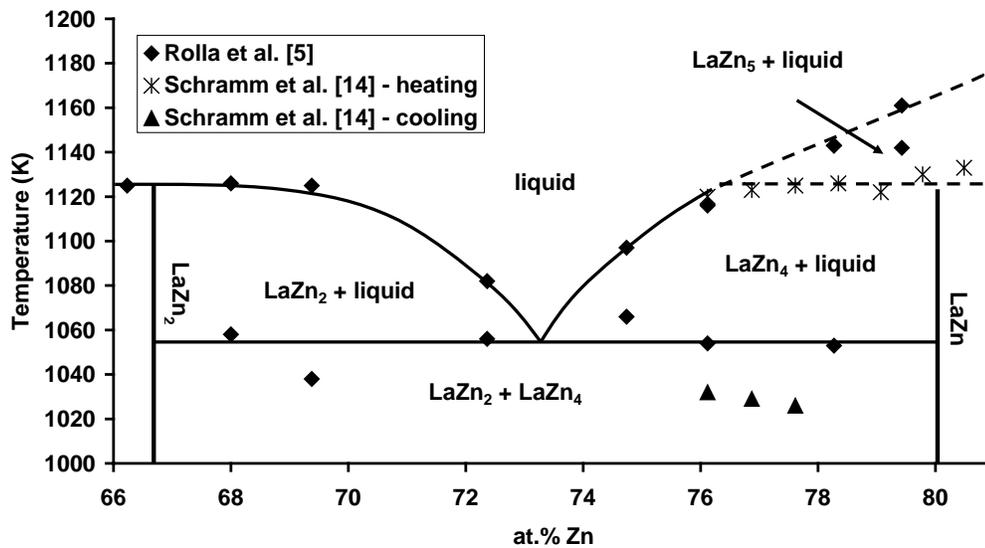
Schramm [14] also observed the eutectic 3 though at the temperature of 1029 K. However, the observed temperature

Table 2. Investigations on the La-Zn Phase Diagram

Experimental Method	Studied Ranges		Ref.
	Temperature (K)	Composition (at. % Zn)	
Direct Thermal Analysis (heating) -TA	600 - 1250	0 - 100	[5]
Direct Thermal Analysis (heating and cooling) -TA	600 - 1250	75 - 100	[14]
Differential Thermal Analysis (heating) - DTA	900 - 1150	66.7	[10]
E.m.f. measurements	700 - 1000	97 - 100	[22]

Table 3. Invariant Reactions in the La-Zn System

Reaction Type	Reaction (on Cooling)	Invariant Compositions and Temperatures		Ref.
		At. % Zn	T (K)	
Eutectic 1	liquid = fcc-La + LaZn	22.0	803	[5]
Congruent melting -LaZn	liquid = LaZn	50.0	1088	[5]
Eutectic 2	liquid = LaZn + LaZn ₂	56.5	1033	[5]
			1047 ?	[10]
Congruent melting - LaZn ₂	liquid = LaZn ₂	66.7	1128	[5]
			1125	[10]
Eutectic 3	liquid = LaZn ₂ + LaZn ₄	73.4	1055	[5]
Decomposition of LaZn ₄	Uncertain	80.0	1144	[5]
Decomposition of LaZn ₅	Uncertain	83.3	1137	[5]
Peritectic decomposition-La ₃ Zn ₂₂	La ₂ Zn ₁₇ + liquid = La ₃ Zn ₂₂	88.0	1205	[14]
Congruent melting - La ₂ Zn ₁₇	liquid = La ₂ Zn ₁₇	89.5	1247	[5]
			1235	[14]
Decomposition of LaZn ₁₁	Uncertain	91.6	983	[14]
Decomposition of LaZn ₁₃	Uncertain	92.8	1113	[5]
			1113	[14]
Invariant 4	liquid = (Zn) + LaZn ₁₃	≈100	688	[14]
			≈100	694

**Fig. (1).** The La-Zn phase diagram from 66 to 81 at.% Zn.

might be underestimated as it was determined on cooling. Therefore we will discard this value.

Eutectic 4 was found by Schramm [14] and Rolla *et al.* [5] at 688 K and 694 K, respectively. No reaction was attributed to this eutectic. However as the reference melting point of Zn (692.73 K) provided by SGTE [21] lies within the range 688-694K, two possibilities can be envisaged. This reaction could either correspond to a eutectic or a degenerated peritectic. Additional investigations are necessary to firmly conclude on the characteristics of this invariant reaction.

Liquidus Curve

Rolla *et al.* [5] are the only authors who performed measurements in the composition range 0-66 at. % Zn (Fig. 2). As mentioned before, due to the low purity of the lanthanum used in the synthesis of the samples, the results in the La-rich domain are not reliable.

Both Rolla *et al.* [5] and Schramm [14] investigated the composition range 66-89 at. % Zn. All the available data are presented in Fig. (3). As the liquidus curves obtained by these authors between 76 and 84 at. % Zn

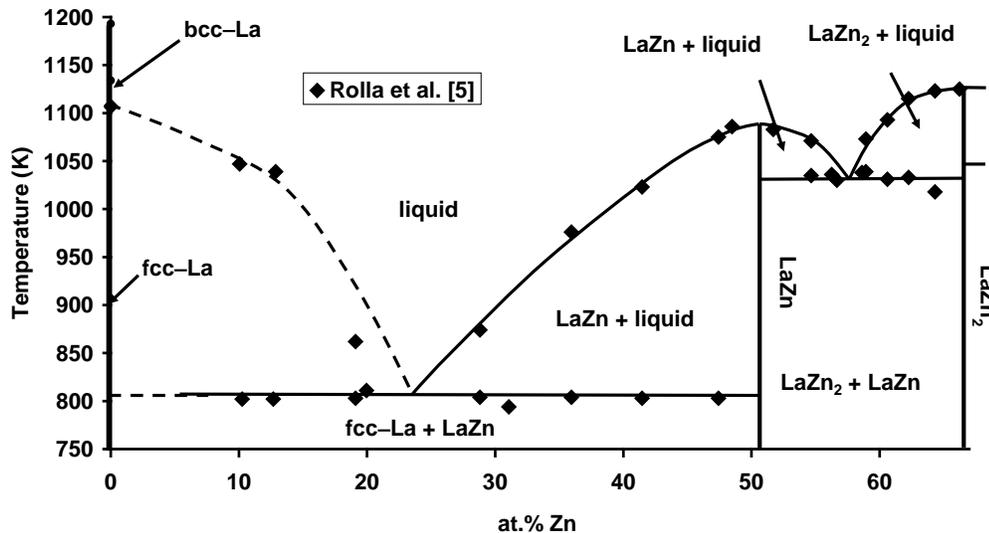


Fig. (2). The La-Zn phase diagram from 0 to 66 at.% Zn.

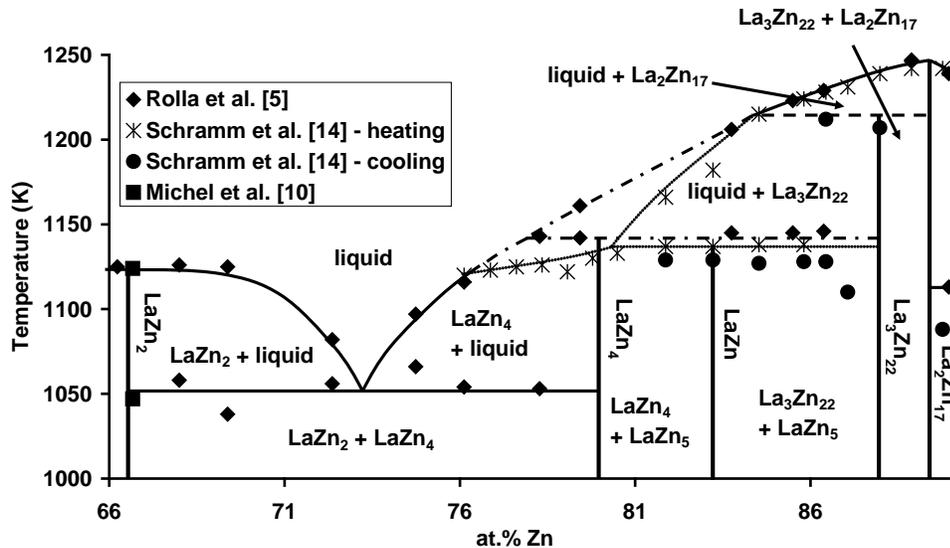


Fig. (3). The La-Zn phase diagram from 66 to 89 at.% Zn.

disagree with each other and because only one compound (either LaZn_4 [5] or LaZn_5 [14]) was considered in each of these works, this part of the phase diagram must be clarified by additional investigations.

The equilibria in the composition range 89-100 at. % Zn are presented in Fig. (4). The liquidus curves determined by Rolla *et al.* [5] and Schramm [14] are in good agreement. In the zinc richest part of this composition domain, the liquidus curve was determined by Lebedev *et al.* [22] from electromotive force (e.m.f) measurements. As expected from the large difference in temperature (about 400K) between the melting point of an alloy with 98 at.%Zn and that of pure zinc, we can notice a very sharp slope for this curve (about $300 \text{ K (at. \%)}^{-1}$). In such a case, only e.m.f measurements are able to provide reliable liquidus curve.

In conclusion, from all the literature data, the phase diagram depicted in Fig. (5) can be proposed. However some discrepancies still remain and accurate, additional experimental investigations are needed to provide a clear picture of the La-Zn phase diagram.

These investigations should focus on the La-rich part of the phase diagram (up to 25 at. % Zn) which is still unknown, on the determination of the temperature of the eutectic 2 (liquid = $\text{LaZn} + \text{LaZn}_2$), on the elucidation of the existence of LaZn_4 and LaZn_5 phases, on the liquidus curve in the composition range 75-89 at. % Zn and finally on the stability ranges of LaZn_{11} and LaZn_{13} .

THERMODYNAMIC DATA

All the thermodynamic investigations on solid phases reported in literature are listed in Table 4.

E.m.f. measurements were performed in the temperature range 700-1000 K in the zinc rich part of the La-Zn phase diagram [23-25]. All the results are plotted in Fig. (6). An overall agreement is observed. Except for Mullayanov *et al.* [24] who indicated a composition range of 95.0-98.6 at. % Zn for their alloys, the other authors did not give values for the studied compositions. According to the La-Zn phase diagram, at those temperatures and for compositions higher than about 93 at.% Zn, the alloys are constituted of a liquid in equilibrium with the solid phase LaZn_{13} . However in their

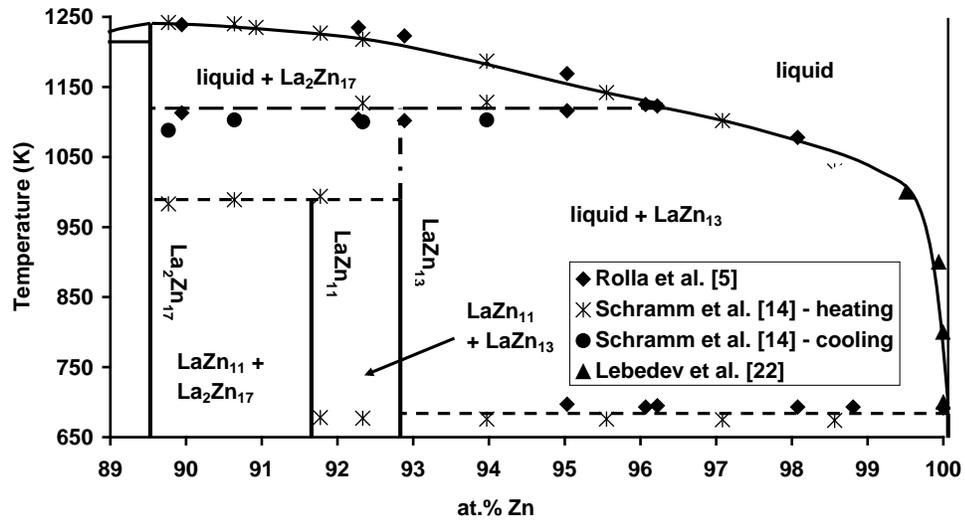


Fig. (4). The La-Zn phase diagram from 89 to 100 at.% Zn.

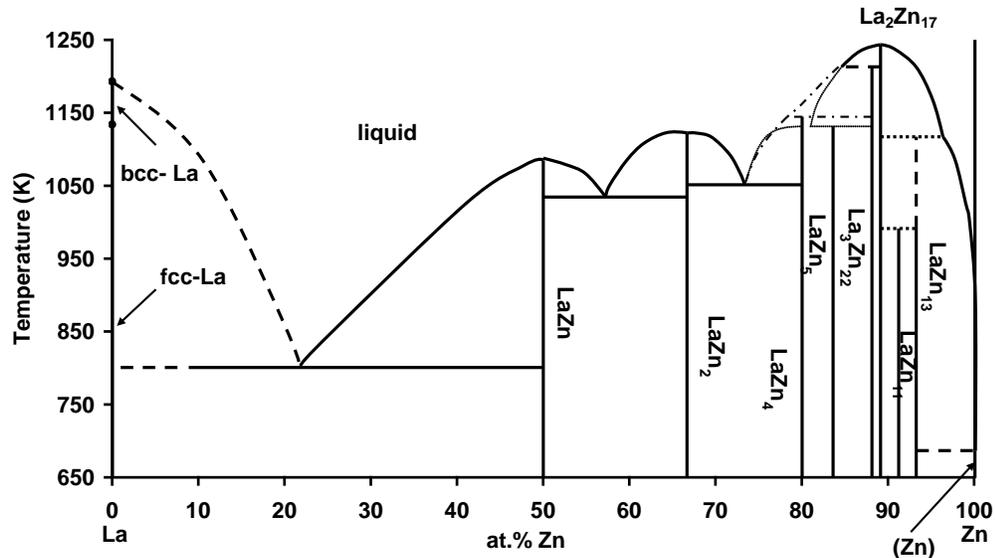


Fig. (5). Most reliable phase diagram after critical review of the literature data.

Table 4. Thermodynamic Investigations in the La-Zn System

Investigation Method	Temperature Range (K)	Studied Phases	Ref.
e.m.f.	730 - 1030	LaZn, LaZn ₂ , LaZn ₄ , LaZn ₅ , La ₃ Zn ₂₂ , La ₂ Zn ₁₇ , LaZn ₁₁	[19]
e.m.f.	720 - 870	LaZn ₁₃ + liquid	[23]
e.m.f.	870 - 1020	LaZn ₁₃ + liquid	[24]
e.m.f.	700 - 800	LaZn ₁₃ + liquid	[25]
Solution calorimetry (in liquid tin)	298	LaZn, LaZn ₂ , LaZn ₄ , LaZn ₅ , La ₃ Zn ₂₂ , La ₂ Zn ₁₇ , LaZn ₁₁ , LaZn ₁₃	[26]
DFT calculations	0	LaZn, LaZn ₂ , LaZn ₅ , La ₂ Zn ₁₇	[26]
Solution calorimetry (in HCl) Relaxation method	2 - 300	LaZn ₁₃	[27]
Direct calorimetry	745	liquid	[28]

papers, the authors attributed the solid phase to LaZn₁₁. This mistake is caused by the fact that the authors did not perform samples analyses and based the interpretation of their results

on a wrong phase diagram. The partial enthalpy, entropy and Gibbs energy of lanthanum determined from these e.m.f. measurements are reported in Table 5.

Kovalevskii *et al.* [19] investigated by e.m.f. measurements the whole range of compositions of the La-Zn phase diagram at 1000 K. The interpretation of these results in the light of previous literature data led the authors to consider seven stable compounds, namely LaZn, LaZn₂, LaZn₄, LaZn₆, LaZn₈, LaZn₉ and LaZn₁₁. However this interpretation disagrees with our analysis regarding the phase stoichiometry. A new interpretation of Kovalevskii's results at 1000 K was presented in Ref. [26]. This interpretation of e.m.f. measurements is in agreement with our suggested phase diagram. The differences between these two interpre-

tations for Kovalevskii's results could be explained by zinc evaporation in the zinc richest samples.

In the same study, Kovalevskii *et al.* [19] investigated the evolution of the e.m.f. with respect to temperature for alloys selected from each two-phase region. The investigated temperatures ranged from 700 to 1120 K. From these data, the partial Gibbs energies of lanthanum are calculated at 1000 K (see Table 5). Table 6 gives the partial enthalpies and entropies determined from the new interpretation of Kovalevskii's measurements [26].

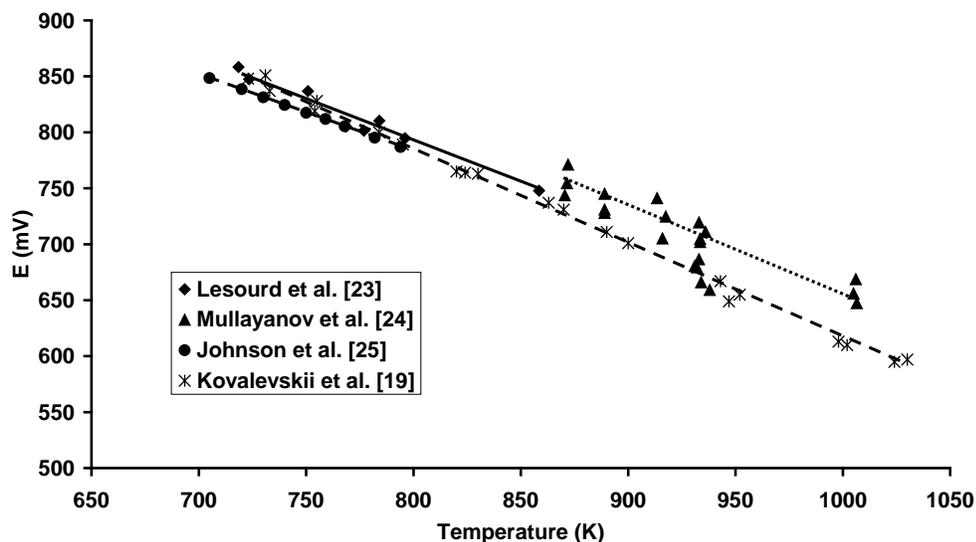


Fig. (6). E.m.f. measurements on two-phase (liquid+solid) alloys belonging to the zinc-richest part of the phase diagram with respect to temperature.

Table 5. Partial Enthalpy, Entropy and Gibbs Energy of Lanthanum Determined from e.m.f Measurements. The Partial Gibbs Energy is Calculated at T

$\overline{\Delta H}_{La}$ (kJ Mol Atom ⁻¹)	$\overline{\Delta S}_{La}$ (J Mol Atom ⁻¹ K ⁻¹)	$\overline{\Delta G}_{La}$ (kJ Mol Atom ⁻¹)	T (K)	Ref.
- 387.4	- 200.8	- 186.6	750	[25]
- 407.5 ± 25.1	- 223.4 ± 33.5	- 246.0 ± 2.5	800	[23]
- 391.3 ± 0.7	- 223.4 ± 0.8	- 167.9 ± 1.5	1000	[22]
- 393.8 ± 5.9	- 216.5 ± 14.2	- 177.2 ± 0.8	1000	[19]

Table 6. Partial Enthalpy, Entropy and Gibbs Energy of La Calculated at 1000 K from the New Interpretation of the Kovalevskii *et al.* Measurements [19] by Berche *et al.* [26]

at. % Zn	$\overline{\Delta H}_{La}$ (kJ Mol Atom ⁻¹)	$\overline{\Delta S}_{La}$ (J Mol Atom ⁻¹ K ⁻¹)	$\overline{\Delta G}_{La}$ (kJ Mol Atom ⁻¹)
91.60 to 99.51	- 394.1 ± 5.9	- 216.7 ± 14.2	- 177.4 ± 0.8
89.50 to 91.60	- 239.7 ± 3.3	- 79.5 ± 18.8	- 160.2 ± 0.8
88.00 to 89.50	- 171.1 ± 13.3	- 53.1 ± 14.2	- 118.0 ± 3.3
83.30 to 88.00	- 90.0 ± 13.4	+ 4.6 ± 13.0	- 94.6 ± 3.3
80.00 to 83.30	- 72.4 ± 10.9	+ 8.8 ± 11.7	- 81.2 ± 3.3
66.67 to 80.00	- 61.5 ± 9.2	- 2.9 ± 9.6	- 58.6 ± 3.3
50.00 to 66.67	- 6.7 ± 2.5	+ 5.4 ± 11.7	- 12.1 ± 1.3
0.00 to 50.00	0.0	0.0	0.0

Morishita *et al.* [27] investigated the thermodynamic properties of the LaZn_{13} phase. The sample was synthesized from pure elements (Zn, 99.9 wt. % and La, 99.99 wt. %) in a high-frequency induction melting furnace. According to the microprobe and X-ray diffraction analyses, a single phase material was obtained. The enthalpy of formation of this sample was measured at 298 K by calorimetry in a 5 N hydrochloric solution. By using a relaxation method, these authors also measured the heat capacity of the sample in the temperature range 2-300 K. The Gibbs energy of LaZn_{13} at 298 K was deduced from these results by Morishita and co-workers.

Recently, Berche *et al.* [26] determined the heat content $H^T - H^{298}$ of $\text{La}_2\text{Zn}_{17}$ between room temperature and 665 K using the drop calorimetry method. A comparison between this value and that obtained using the Kopp-Neumann rule suggests a negligible excess heat capacity (see Table 7).

Table 7. Heat Contents of $\text{La}_2\text{Zn}_{17}$

T (K)	$H^T - H^{298}$ (kJ (Mol of Atom) ⁻¹)	
	Calorimetry	Kopp-Neumann
665	9.1 ± 0.6 ¹	10.0
910	15.2 ± 0.3 ²	16.7

¹experiment; ²linear extrapolation of experimental results from 665K to 910K.

In the same study, Berche *et al.* [26] performed solution calorimetry measurements at 665 K in tin bath to determine

the enthalpies of formation of the La-Zn intermediate phases at 298 K. The result obtained for LaZn_{13} agrees with Morishita's value [27] within the uncertainty limit (see Fig. 7). The enthalpies of formation of LaZn , LaZn_2 , LaZn_5 and $\text{La}_2\text{Zn}_{17}$ were also calculated at 0K by Berche *et al.* [26] using Density Functional Theory (DFT) calculations. The theoretical results are compared to those obtained experimentally by the same authors in Table 8 and in Fig. (7). A good agreement is observed even though the enthalpies of formation were determined at different temperatures (0K and 298K). This observation could support our previous statement that the excess heat capacity is low for the La-Zn phases. The enthalpy of formation of the intermediate phases of the La-Zn system were also estimated by Berche *et al.* [26] from Kovalevskii's measurements in the temperature range 700–1120 K. The values are given in Table 8. The heat contents and average heat capacities of the La-Zn compounds were then determined by Berche *et al.* [26] for temperatures between 298 K and 910 K. These quantities were deduced from the difference of the enthalpies of formation of the La-Zn compounds between 298 K and 910 K. They are reported in Table 9. Note that 910K corresponds to the average temperature of the temperature range investigated by Kovalevskii. The heat content of $\text{La}_2\text{Zn}_{17}$ reported in Table 9 (12.0 kJ mol^{-1}) is in relative good agreement with that reported in Table 7 ($15.2 \pm 0.3 \text{ kJ mol}^{-1}$) which was obtained from linear extrapolation of the experimental values from 665K to 910K.

Finally, the partial enthalpy of mixing of lanthanum in liquid zinc at 745 K was determined by Berche [28] using direct solution calorimetric measurements. The results are

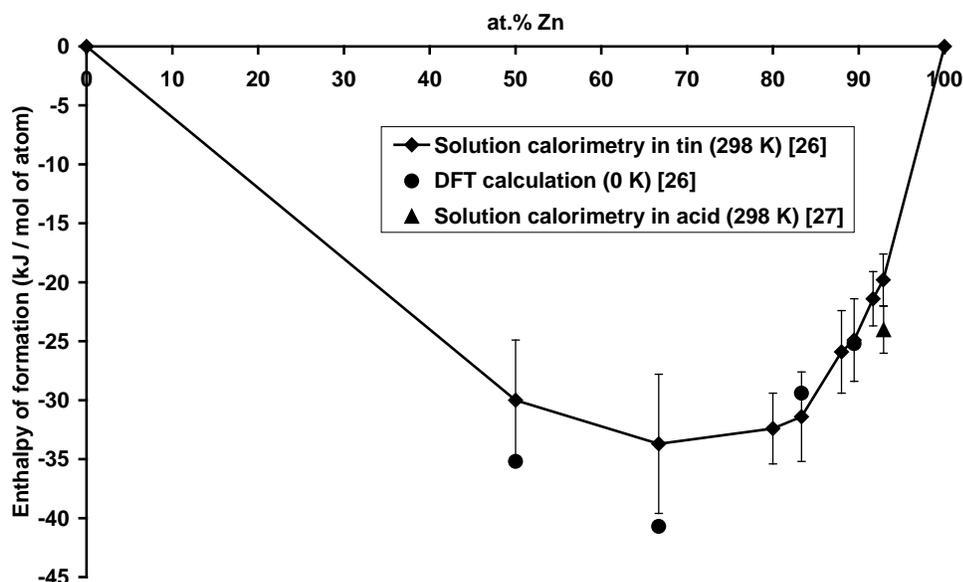


Fig. (7). Enthalpies of formation of solid La-Zn phases at 0 K and 298 K from [26].

Table 8. Enthalpies of Formation of the La-Zn Intermediate Phases (in kJ (Mol of Atom)⁻¹) Determined in [26]

T (K)	LaZn	LaZn_2	LaZn_4	LaZn_5	$\text{La}_3\text{Zn}_{22}$	$\text{La}_2\text{Zn}_{17}$	LaZn_{11}	LaZn_{13}
298	-30.0 ± 5.1	-33.7 ± 5.9	-32.4 ± 3.0	-31.4 ± 3.8	-25.9 ± 3.5	-24.9 ± 3.5	-21.4 ± 2.3	-19.8 ± 2.2
0	-35.2	-40.9	-	-29.4	-	-25.2	-	-
700-1120	-36.2 ± 3.1	-46.1 ± 3.3	-43.0 ± 2.0	-41.8 ± 1.6	-39.1 ± 0.5	-37.1 ± 0.9	-32.2 ± 0.9	-

Table 9. Heat Contents ($H^T - H^{298}$ in kJ Mol^{-1}) and Average Heat Capacities (C_p in $\text{J (Mol of Atom)}^{-1} \text{K}^{-1}$) [26]

	Solid Compounds						
	LaZn	LaZn ₂	LaZn ₄	LaZn ₅	La ₃ Zn ₂₂	La ₂ Zn ₁₇	LaZn ₁₁
$H^T - H^{298}$	15.3	10.3	13.0	13.5	11.0	12.0	13.6
C_p	25.1	16.9	21.3	22.0	17.9	19.6	22.3

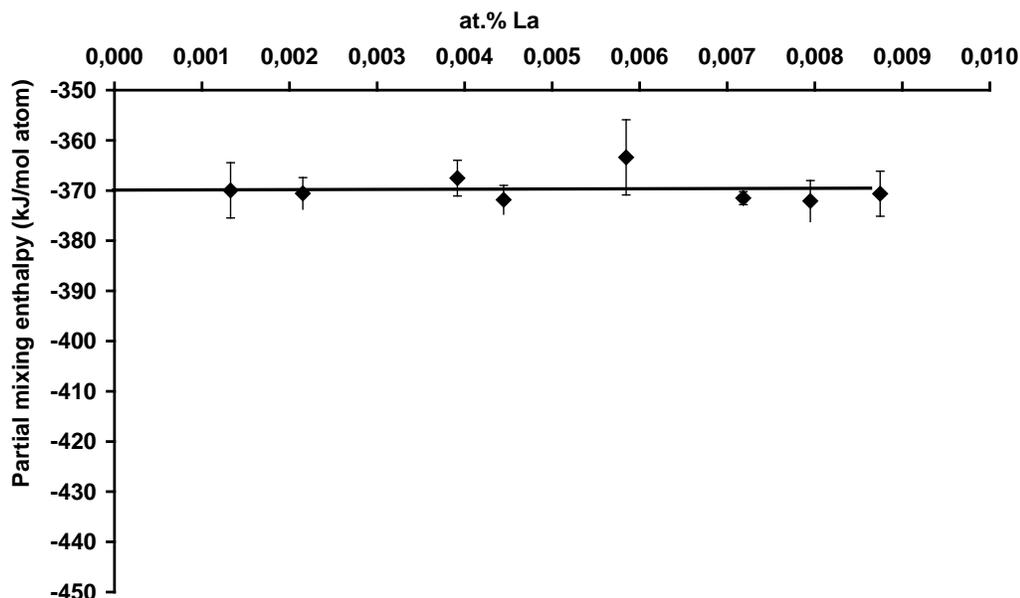


Fig. (8). Partial enthalpy of mixing of lanthanum in liquid zinc at 745 K [28].

presented in Fig. (8). The value of the partial enthalpy of mixing of La in liquid zinc at 745 K at infinite dilution amounts to about $-370 \text{ kJ (mol of atom)}^{-1}$.

CONCLUSION

The La-Zn phase diagram reported in Massalski's compilation [4] is only based on the experimental data of Rolla *et al.* [5]. In this work, we propose a new phase diagram that accounts for the whole reliable set of data available in literature. Even though the description of this phase diagram is incomplete and because some doubts remain due to discrepancies between the literature data, the main phase equilibria are described.

Among the eight solid compounds LaZn, LaZn₂, LaZn₄, LaZn₅, La₃Zn₂₂, La₂Zn₁₇, LaZn₁₁ and LaZn₁₃, only LaZn₁₃ presents a nonstoichiometric domain. LaZn, LaZn₂ and La₂Zn₁₇ melt congruently whereas La₃Zn₂₂ decomposes peritectically. The reactions involving each of the LaZn₄, LaZn₅, La₃Zn₂₂, LaZn₁₁ and LaZn₁₃ phases deserve new investigations. New measurements are also required in the La- and Zn-rich regions and the characteristics of the eutectic equilibrium "liquid = LaZn + LaZn₂" must be clarified. Furthermore, the compositions range 76–86 at. %Zn must be reinvestigated.

Regarding the thermodynamic data, they have already been determined for solid phases. However, only a few thermodynamic information is available on the liquid phase.

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